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CATHODE CATALYST FOR PRIMARY PHOSPHORIC ACID FUEL CELLS:

5TH QUARTERLY REPORT

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1.0 Objective and Scope of Work

1.1 Bond Stability

The objective of the program is to evaluate the stability of three ligands useful to covalently link cobalt TAA to the surface of carbon. The link length of the most stable ligand will be varied to determine the effect on bonded-CoTAA catalytic activity. A cathode will be prepared of the most stable and active ligand form and tested for one month in a 150°C primary fuel cell. Five tasks will be carried out to obtain the data required to meet these objectives:

1. Functionalize the surface of Vulcan XC-72 with three ligand types (acylation, cycloaddition, alkylation);
2. Quaternize the ligands with a ^{14}C -labeled amine and monitor the rate of ^{14}C release to determine the most stable ligand type;
3. Prepare carbon with varying link lengths of the most stable ligand type and react it with bis-aminated TAA;
4. Metallate the bonded-TAA and determine electrocatalytic activity;
5. Test the three most active link-lengths as wetproofed cathodes in primary fuel cells.

1.2 Improve Catalyst Performance

The electrical conductivity and the activity of TAA may be improved by use of dimeric face-to-face TAA with four two-carbon bridges. Once prepared, the dimeric TAA will be metallated and evaluated in a 150°C primary fuel cell.

2.0 Summary of Progress to Date

2.1 Bond Synthesis

Four different carbon functionalization procedures have been carried out: acylation, cycloaddition and two types of alkylation. Based on the release ^{14}C from these carbons, after reaction with ^{14}C -labeled dimethylamino TAA and metallation with cobalt, the alkylation procedures have been identified as providing bonded CoTAA of greatest stability over a thirty day test period in 150°C 85% phosphoric acid. These chemical results have been confirmed based on cyclic voltammetry and pulse voltammetry.

2.2 Effect of Link Length

Vulcan XC-72 has been functionalized via an alkylating procedure to obtain CoTAA bonded to the surface of carbon by four different link lengths (3,4,5 and 6 carbons); no significant initial difference in performance has been observed based on pulse voltammetry as a function of link length.

2.3 Dimeric TAA

Two types of dimeric CoTAA have been prepared. Initial screening by pulse voltammetry show them to be active catalysts.

2.4 PTFE Stability

Four commercially available PTFEs have been shown to be chemically and physically stable after 120 days in 200°C 85% phosphoric acid. Stressing electrochemically in 150°C 85% phosphoric acid has also shown no effect after 30 days.

2.5 Half-Cell Evaluation

Half-cell tests have shown that CoTAA-bonded to carbon

via an alkylating procedure is a more active catalyst than is platinum based on a factor of two improvement in Tafel slope. Half-cell tests have also shown that bonded-CoTAA catalysts do not suffer a loss in potential when air is used rather than oxygen.

2.6 PTFE Preparation

A procedure to polymerize TFE has been identified and product obtained.

3.0 Technical Progress in the Fifth Quarter

3.1 Half-Cell Cathode Evaluation

3.1.1 Cathode Preparation

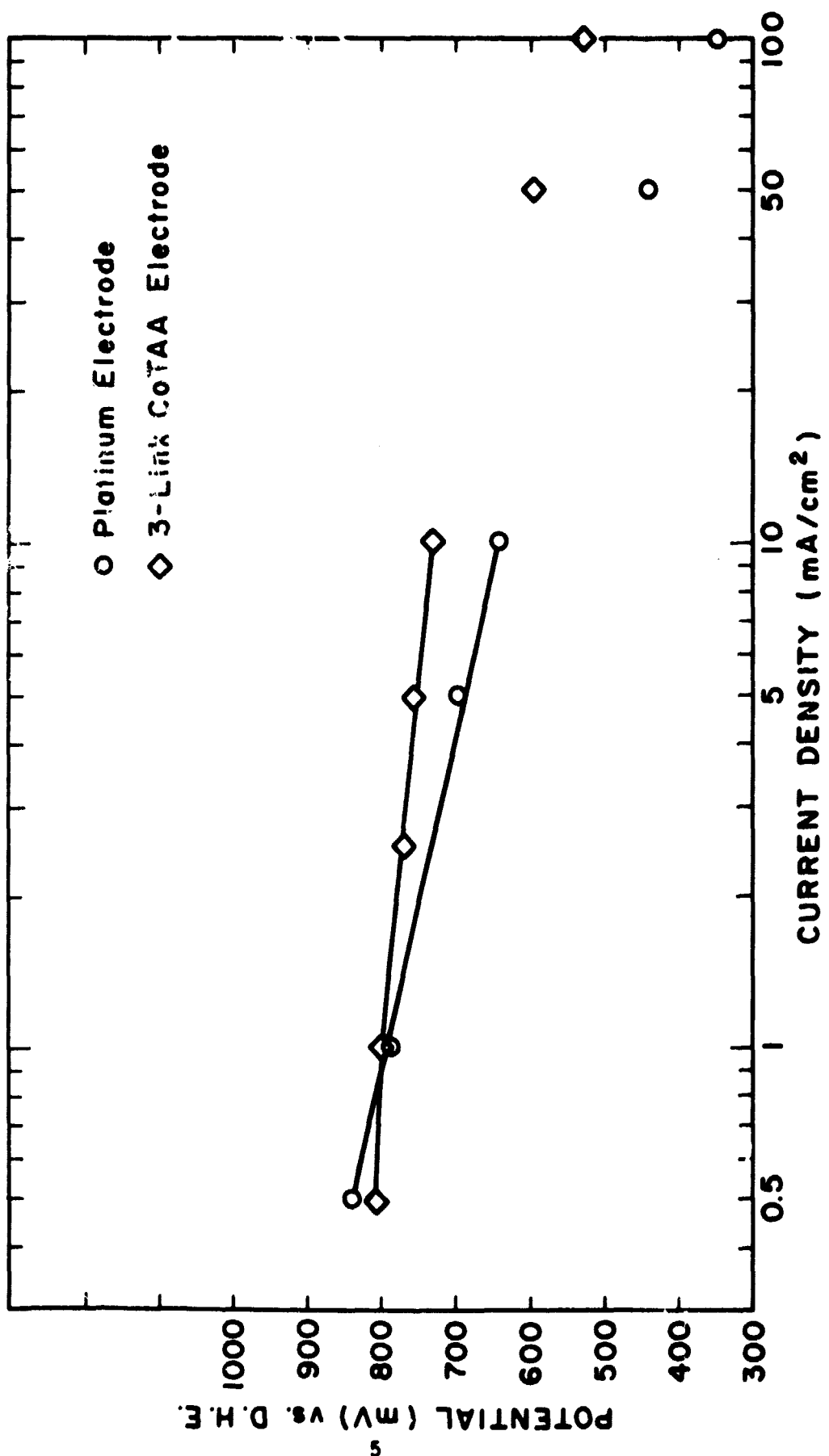
Wet-proof cathodes were prepared by depositing 100 mg of 30%/70% Teflon/catalyzed carbon on a support of stiff carbon fabric (PWB-35; Stackpole Fibers) containing a thin layer (100 mg) of 30%/70% Teflon/Vulcan XC-72. The matrix was placed on a gold-plated expanded tantalum screen and pressed at 320°C/1000 psi for 5 min. Two control cathodes were prepared: an uncatalyzed Vulcan XC-72 cathode and a 10% platinum on carbon catalyzed cathode (Protech; 50-25 Å crystals; 120-150 m²/g).

3.1.2 Short-Term Tests

Six types of catalyzed cathodes were tested in 100°C 85% phosphoric acid. After initial performance evaluation the cathodes were held at +650 mV vs DHE for 100 hours and performance was again evaluated. The six cathode types were 10% platinum on carbon, 33% CoTAA on Vulcan XC-72, 33% dimeric CoTAA on Vulcan XC-72, 33% CoTAA on Vulcan XC-72 reacted to have CoTAA linked via a three carbon link on the surface, 33% CoTAA on Vulcan XC-72 with four-carbon linked CoTAA, and 33% CoTAA on Vulcan XC-72 with five-carbon linked CoTAA. All the CoTAA-containing carbons were sintered for two hours under nitrogen at 700°C prior to cathode fabrication; the alkylation procedure was used to provide the carbon links.

Provided in Figure 3.1 is a Tafel plot for the IR-free data obtained for the platinum control and for the 33% CoTAA

Figure 3.1 : Electrode Performance at 100 °C in 85% H_3PO_4
After 100 Hours.



sintered on three-carbon linked CoTAA-Vulcan XC-72. Provided in Table 3.1 is a summary of the IR-free performance data obtained for the six cathode types after stressing for 100 hours in 100°C 85% phosphoric acid at +650 mV vs a DHE. Based both on the Tafel slope (mV/decade) and on the absolute magnitude of the potential at 10 mA/cm² using 99.95% oxygen as the fuel, all of the sintered CoTAA (linked or non-linked) cathodes show significantly improved performance compared to the 10% platinum-catalyzed cathode; the dimeric-CoTAA catalyzed cathode showed performance similar to platinum. The rest potential of all the CoTAA-catalyzed cathodes was approximately 130 mV lower than that of the platinum catalyzed cathode.

A seventh cathode was run which was catalyzed with 33% diazodimeric CoTAA (sintered); this cathode was stressed for 100 hours at 125°C. Shown also in Table 3.1 are the IR-free data obtained on this cathode; its performance was similar to that of the dimeric cathode at 100°C.

During the 100 hour stress period, the performance of none of the seven cathodes shown in Table 3.1 showed any significant change (less than 1%). Two of the cathodes (diazodimeric CoTAA and C-4/CoTAA) were allowed to continue for an additional 900 hours. During this extended test period, the performance of these two was observed to decay uniformly (approximately 17% and 22% respectively) despite the 25°C temperature difference. Raising the temperature to 125°C for the bonded cathodes (C-4, C-5) or the unbonded CoTAA resulted in

Table 3.1

Performance of Various Cathodes
after 100 hours*

<u>Catalyst</u>	<u>Rest Potential in O₂ at 100°C (mV)</u>	<u>Tafel Slope at 100°C (mV/decade)</u>	<u>Potential at 10 mA/cm² (mV)</u>
Platinum	960	130	640
CoTAA	830	60	758
Dimeric CoTAA	813	180	540
Diazo Dimeric CoTAA	821	160	590
C-3/CoTAA	833	60	750
C-4/CoTAA	840	60	740
C-5/CoTAA	816	50	730

* Cathodes held at 100°C at 650 mV vs DHE during test period except for the diazo dimeric CoTAA which was held at 125°C.

increased decay in performance (21%, 46% and 68% respectively) in approximately 100 hours. Based on the observation that the electrolyte was colored a dark amber when increased decay was observed, the C-3 cathode was tested under a different condition. For this cathode, the electrolyte contained 3 mg/ml of cobalt phosphate ($\text{Co}_3 (\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$); the cathode was stressed at 125°C in 85% phosphoric acid and + 650 mV vs DHE. After 100 hours at these conditions, no performance decay was observed. This suggests that the performance decay mechanism is dissolution of the cobalt species from the organo metallic complex; the solution to this problem is apparently increasing solution cobalt content.

3.1.3 Effect of Fuel Variation

An examination was made of the effect of using compressed air rather than oxygen as the fuel source. Three cathodes were examined: a commercially available platinum catalyzed cathode (RA2-Prototech, Inc., Newton Highlands, MA), a platinum catalyzed cathode made at ECO (10% platinum on carbon), and a C-5/CoTAA catalyzed cathode. These latter two cathodes were prepared as described in Section 3.1.1 above.

The cathodes were tested at 100°C in 85% phosphoric acid. The results obtained are provided in Table 3.2; these results show that the platinum catalyzed cathodes have a rest potential loss from using air rather than oxygen which is on the order of 70 mV; the C-5/CoTAA does not have such a loss. This difference in loss is also observed under load when the two ECO prepared cathodes are compared. Thus, CoTAA cathodes do not appear to

Table 3.2

Cathode Performance on Air vs Oxygen*

Cathode	Potential, mV				
	<u>Load</u> , mA/cm ²	0		2.5	
		<u>Gas</u>	<u>Gas</u>	<u>Gas</u>	<u>Gas</u>
RA2-Pt		O ₂	Air	O ₂	Air
		974	894	886	828
Pt		884	828	740	640
C-5/CoTAA		828	828	784	744

* at 100°C in 85% phosphoric acid; potential measured vs DHE.

3.2 PTFE Evaluation

3.2.1 Effect of Phosphoric Acid

Films were formed of four commercially available PTFE powders; these films (dia. 1.32 cm; thickness 0.8 mm) were stressed in 200°C 85% phosphoric acid. The films were held in Teflon stoppered quartz tubes to minimize water loss; make up water was added weekly. The four films have been examined monthly for physical size changes, for wetting angle changes and for changes in film IR. No changes have been observed after four months of stressing.

3.2.2 Electrochemical Stressing

A second series of films were prepared; these films were held in close contact to slightly smaller diameter disks of vitreous carbon by wrapping with platinum wire. These disks were suspended in 85% phosphoric acid at 150°C. In the vessel was inserted a counter electrode (a 2 cm² platinum flag) and a quartz-tipped oxygen bubbler. The disks were held at + 200 mV vs DHE; make up water was added as needed.

After one month of stressing, no obvious changes have occurred in film structure.

3.2.3 PTFE Synthesis

Polymerization of TFE has been accomplished under pressure (380 psi) in water using a ammonium persulfate initiator. A sample of TFE was introduced into a 75 ml stainless steel bomb containing 50 ml of deoxygenated distilled water and 100 mg of ammonium persulfate; the bomb was placed

in a rocker and heated to an internal temperature of 80°C. The pressure was observed to go from 380 psi to 130 psi. The bomb was cooled, opened and the product scraped out and collected by filtration from the aqueous solution: 3.3 gm of an off-white powder was obtained.